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Epoxies as Composite Matrices*

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Introduction

High-performance epoxy-graphite or epoxy-boron fiber composites are often utilized in extreme service environments, particularly in the aerospace industry. A number of laboratory and field studies have indicated that the combined effects of sorbed moisture and thermal environment can cause significant changes in the mechanical response of these materials [1,2]. The long-term, in-service durability of epoxy composites is unknown primarily because:

(1) long-term, in-service aging characteristics are difficult to simulate by short-term laboratory and/or field tests, and

(2) the basic phenomena responsible for the changes in the epoxy matrix, the epoxy-fiber interfacial region, and the overall mechanical response of the composite have not all been identified and/or understood.

There are three basic areas necessary for meaningful epoxy durability predictions:

(1) the structure of epoxies, their modes of deformation and failure, and the structural parameters controlling these modes;

(2) the effects of sorbed moisture on the epoxy structure, properties, and modes of deformation and failure; and

(3) the complex fabrication and environmental phenomena affecting the durability in service environments.

Experimental

Material

The primary epoxy system considered in this paper is diaminodiphenyl sulfone (Ciba-Geigy, Eporal)-cured tetraglycidyl 4,4′ diaminodiphenyl methane (Ciba Geigy, MY720) epoxy (TGDDM-DDS). The structures of the unreacted TGDDM epoxide and DDS amine monomers are illustrated in Fig. 1. This TGDDM-DDS epoxy system is the primary matrix utilized in aerospace high-performance epoxy-fiber composites.
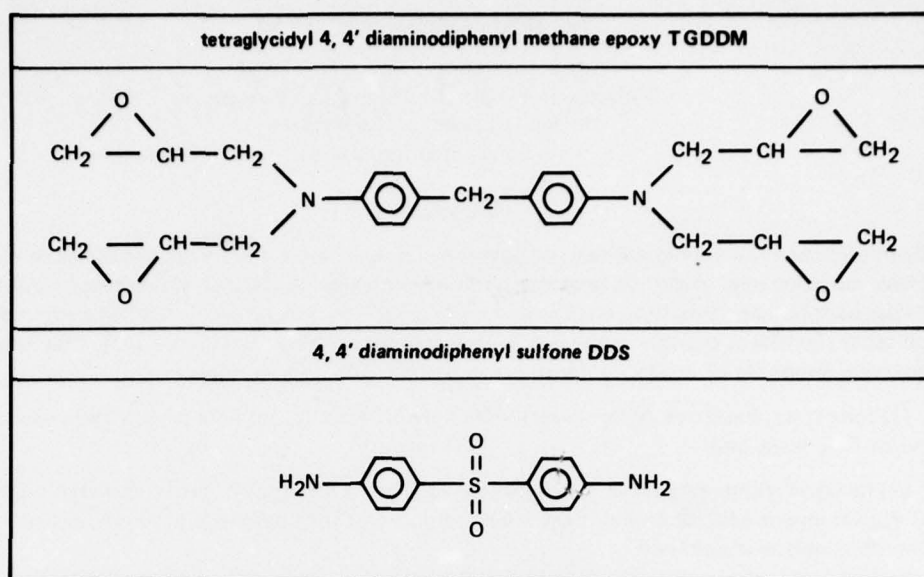
Experiments

TGDDM-DDS epoxy specimens suitably shaped for tensile mechanical property, fracture topography, x-ray emission spectroscopy, and density measurements were prepared in silicone rubber molds and cured for 1 h at 150°C and 5 h at 177°C. Thinner epoxy films for physical structure studies by bright-field transmission electron microscopy and electron diffraction studies were prepared between salt crystals. TGDDM-DDS epoxies of various initial compositions (10-35 wt% DDS) exposed to various environments were investigated.

A table-model tensile tester (Instron TM-S-1130) was used to determine the mechanical properties. An electron microscope (JEOL model JEM 100B) was used in the scanning mode for fracture topography and x-ray emission spectroscopy studies and in the transmission mode for the diffraction and bright-field studies. An optical microscope (Zeiss Ultraphot II) was also used for fracture topography studies. Density measurements were performed on a Mettler M-5 microbalance.

Figure 1 The TGDDM-DDS epoxy system.

Results and Discussion

Structure-Property Studies

The major structural parameters controlling the modes of deformation and failure and the mechanical response of epoxies are the crosslinked network structure and the microvoid characteristics [3-11].

Generally, the cure process and final network structure of epoxies have been estimated from the chemistry of the system, if the curing reactions are known and assumed to go to completion, and experimental techniques such as infrared spectra, swelling, dynamic mechanical, thermal conductivity, and differential scanning calorimetry measurements [12-26]. However, in many epoxy systems, the chemical reactions are diffusion controlled and incomplete and there is a heterogeneous distribution in the crosslink density.

The TGDDM-DDS epoxy system, cured at $177^\circ C$, is not highly crosslinked despite the tetra-functionality of the TGDDM epoxide. We have monitored the tensile mechanical properties of the TGDDM-DDS epoxy system as a function of composition (10-35 wt% DDS) and test temperature (23°-$250^\circ C$). Figure 2 is a plot of tensile strength, ultimate elongation, and Young's modulus from 23°-$250^\circ C$ for a TGDDM-DDS (35 wt% DDS) epoxy. The gradual decrease in tensile strength and modulus and the increase in ultimate elongation from 200°-$250^\circ C$ suggests that a broad glass transition exists in this temperature range. Ultimate extensions of $\geqslant 15\%$ near T_g for epoxies with 15-35 wt% DDS suggests these glasses are not highly crosslinked.

A plot of T_g versus initial DDS concentration, shown in Fig. 3, confirms that these epoxies are not highly crosslinked. [The temperatures representative of these broad T_g's were taken as those temperatures at which the room-temperature modulus (E_{RT}) decreased by half (i.e., $E_{RT}/2$)]. From 10-25 wt% DDS, the T_g rises with increasing DDS concentration because of corresponding increases in molecular weight and/or crosslink density. The T_g exhibits a maximum of $\sim 250^\circ C$ at ~ 30 wt% DDS and subsequently decreases for higher DDS concentrations. For epoxies prepared from > 25 wt% DDS, steric and diffusional restrictions evidently inhibit additional epoxy-amine reactions. Above ~ 30 wt% DDS concentrations, unreacted DDS molecules plasticize the epoxy system and decrease the T_g. However, 37 wt% DDS is required to consume half the TGDDM epoxide groups when only epoxide/primary-amine reactions occur. Hence, the maximum in T_g at 30 wt% DDS suggests that less than half the TGDDM epoxide groups have reacted when 100% of the DDS is consumed.
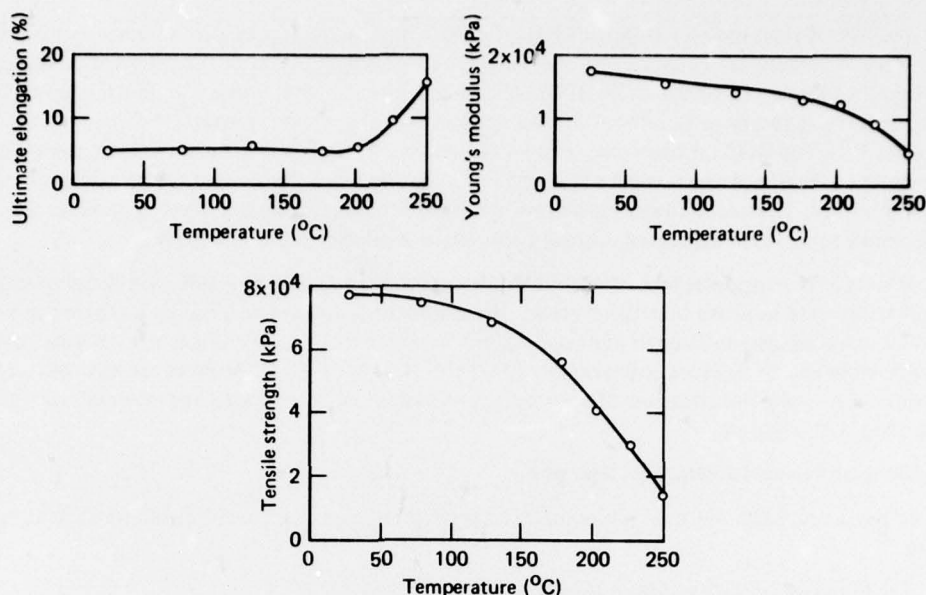
Figure 2 Tensile strength, ultimate elongation, and Young's modulus versus temperature for TGDDM-DDS (35 wt% DDS) epoxy (10^{-2}/min strain rate).
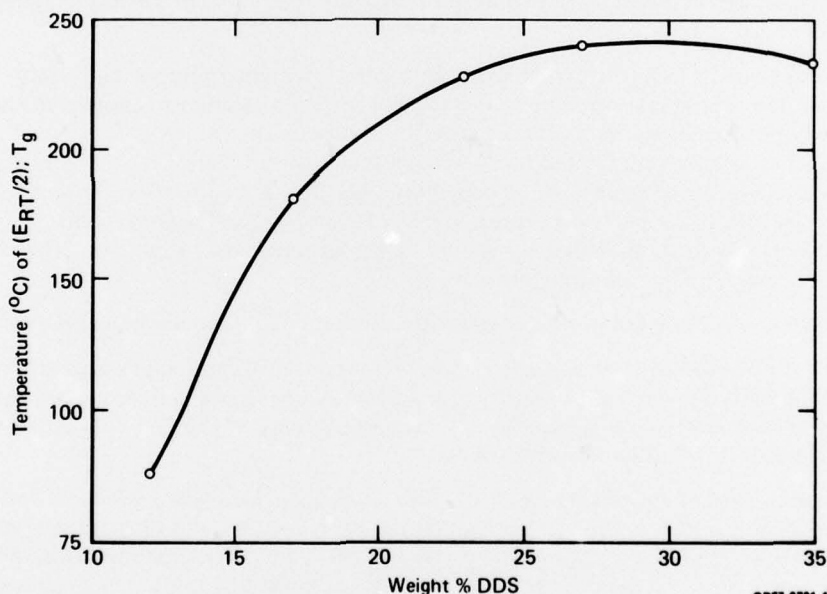
Figure 3 T_g versus initial wt% of DDS in TGDDM-DDS epoxies.

After cure, aggregates of unreacted DDS molecules have been detected in TGDDM-DDS (>25 wt% DDS) epoxies by both electron diffraction and x-ray emission spectroscopy studies. Electron diffraction patterns were obtained from thin films prepared from >25 wt% DDS that were similar to those obtained from the unreacted DDS crystals. The aggregates of unreacted DDS molecules crystallize after cooling the epoxy from its cure temperature. In addition, x-ray emission spectroscopy studies of fracture surfaces have detected regions of high sulfur content which are probably clusters of unreacted DDS molecules.

The TGDDM-DDS epoxy networks consist of regions of high-crosslink density as indicated by bright-field transmission electron microscopy in the 2-15 nm range and by scanning electron microscopy in the 1-5 μm range.

Microvoids can have a deleterious effect on the mechanical properties of epoxies by acting as stress concentrators and also on the durability by serving as a sink for the accumulation of sorbed moisture. To obtain a TGDDM-DDS epoxy system with a high T_g, which is advantageous to limit the deleterious effects of sorbed moisture on this epoxy, requires ~ 30 wt% DDS in the initial TGDDM-DDS mixture (see Fig. 3). However, at these DDS concentrations, aggregates of unreacted DDS molecules can be trapped in the epoxy after the system forms a glass at the cure temperature. Thermal-anneal/moisture-sorption/mechanical-property studies indicate that elimination of these aggregates during cure results a microvoids in the glass.

The fracture topographies of TGDDM-DDS epoxies fractured as a function of temperature and strain-rate indicate that these glasses predominantly deform and fail by a crazing process. These epoxies also deform to a limited extent by shear banding as indicated by regular right-angle steps in the fracture topography. The deformation of TGDDM-DDS epoxies will depend on the size and concentration of any regions of high-crosslink density and the material interconnecting such regions.

Effects of Sorbed Moisture on Epoxies

The pertinent basic physical phenomena in epoxies induced and/or modified by sorbed moisture are

(1) lowering of T_g by sorbed moisture,

(2) diffusion of sorbed moisture,

(3) swelling stresses induced by sorbed moisture, and

(4) modification of the deformation and failure modes and the mechanical response by sorbed moisture.

The sorption of moisture by epoxies lowers their T_g's and correspondingly causes them to soften at lower temperatures. Kelley and Bueche [27] have derived an expression relating the T_g of a polymer-diluent system to that of the T_g's of the two components. This expression assumes that the free volume contributed by the diluent is additive to that of the polymer and that the *free volumes of the mixture and components at their T_g's are a universal constant. However, the* T_g's of TGDDM-DDS epoxy-moisture systems, containing equilibrium amounts of sorbed moisture, are considerably lower than those predicted by the Kelley-Beuche expression. This discrepancy could be caused by the following phenomena:

(1) the strong hydrogen-bonding capability of water could produce anomalous effects or

(2) if the epoxy has a heterogeneous-crosslink density distribution, moisture will preferentially *sorb in regions of low-crosslink density. The regions of low-crosslink density control the flow* processes that occur at T_g. Hence, the depression of T_g may be greater than that expected for a homogeneous distribution of sorbed water.

The durability of epoxies and epoxy-composites in many aerospace service environments depends on the degree of deterioration of the high-temperature mechanical properties caused by the plasticizing effect of sorbed moisture. The previous relative-humidity/time/temperature exposure of the epoxy component and the diffusion characteristics of moisture in this component determine the moisture profile and the resultant mechanical response of the material. Hence, the diffusion characteristics of moisture in an epoxy component are critical factors for predicting mechanical response and durability in a given service environment. Fickian diffusion has been utilized successfully as the controlling mechanism to predict the concentration and distribution of sorbed moisture [28-30] and corresponding deterioration of high-temperature mechanical properties. Moisture sorption can, however, cause formation of permanent damage regions or modification of the epoxy network which will result in deviations from Fickian diffusion and accelerate moisture sorption. These structural modifications can be

(1) bond cleavage or crack formation as a result of swelling stresses and/or relaxation of fabrication stresses,

(2) formation of additional crosslinks by moisture-enhanced mobility of unreacted groups, and

(3) modification of the free volume and/or microvoid characteristics.

Sorbed moisture causes epoxies to swell [1, 31, 32]. The swelling stresses caused by moisture gradients, together with other stresses inherent in the material, such as fabrication stresses, can be sufficiently large to cause localized fracture of the polymer [32]. However, to compute the moisture sorption levels for specific environmental conditions that cause network modification and subsequent growth of permanent damage regions in epoxies requires a detailed knowledge of the network structure and the stress levels in the presence of moisture where damage occurs in the network. This type of information is not yet available.

Sorbed moisture acts as a solvent crazing agent in TGDDM-DDS epoxies. The microscopic yield stress (that stress at the onset of non-linear behavior in the tensile stress-strain curve) is shown in Fig. 4 as a function of test temperature for both initially wet and dry TGDDM-DDS (27 wt% DDS) epoxies. The microscopic yield stress of the wet epoxies is lower than that of the dry glasses from room temperature to 150°C. Above 150°C, the yield stresses of the wet and dry epoxies merge because water is eliminated from the wet specimens during the test. From room temperature to 150°C, the lower yield stresses of the epoxies containing 4 wt% sorbed moisture, relative to those of the dry epoxies, are equivalent to lowering the dry yield stresses 100°-125°C on the temperature scale. However, the T_g of this epoxy is lowered only ∼60°C by ∼4 wt% sorbed moisture. These observations imply that the craze cavitation stress is more susceptible to sorbed moisture than the main T_g. Hence, the magnitude T_g is lowered on the temperature scale by sorbed moisture cannot be utilized to predict any modification of the formation of permanent damage regions in these epoxies. The craze cavitational stress is more sensitive to sorbed moisture than the T_g for a heterogeneous distribution of moisture in the epoxy. High moisture concentrations in localized regions enhance cavitation by plasticization which results in a lower local shear yield stress. The overall T_g of the epoxy, however, is generally measured on a macroscopic level and is not sensitive to high local moisture concentrations. The large mirror-like region and the numerous cavities observed in the fracture topography initiation region of wet epoxies also indicate that the craze initiation and growth processes are enhanced by sorbed moisture.

The ease of diffusion of moisture through a porous craze structure and its accumulation near the craze tip where it enhances cavitation must be considered a significant mechanism for the
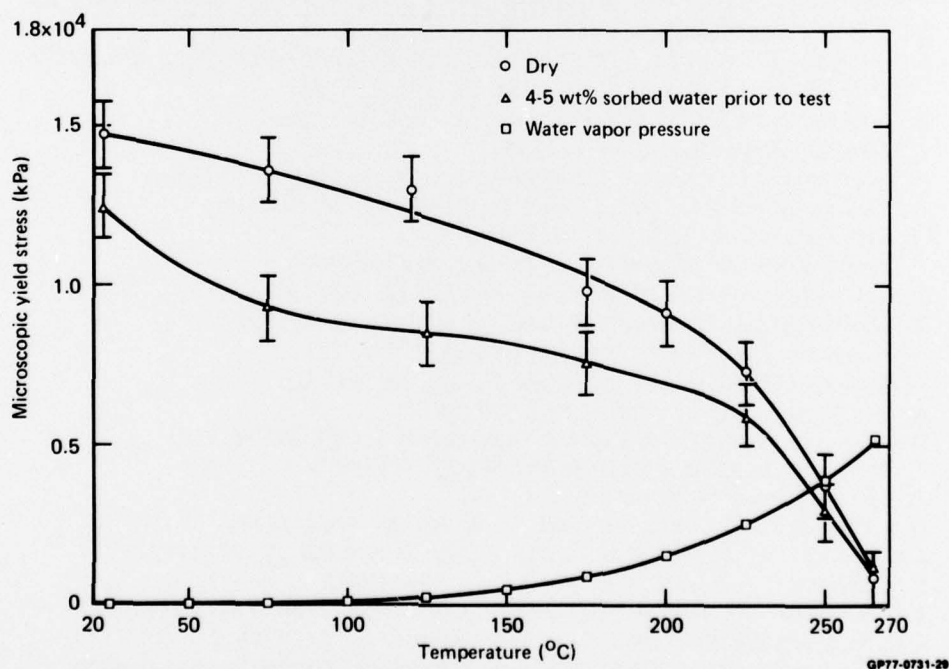

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Figure 4 Microscopic yield stress (strain-rate ∼ 10^{-2}/min) of both initially wet (∼4 wt% sorbed moisture) and dry TGDDM-DDS (27 wt% DDS) epoxies as a function of temperature.

growth of permanent damage regions in these glasses in humid environments, particularly in view of the low stress levels at which cavitation generally occurs in polymer glasses.

Factors that Control the Durability of Epoxies

In the service environment, the durability of epoxies depends on a complex number of interacting phenomena. The factors that control the critical path to ultimate failure or unacceptable damage depend specifically on the particular environmental conditions. In the presentation, all possible factors that generally effect the durability of epoxies in service environments are reviewed, and some of the critical environments that affect the durability of epoxies and the difficulties in predicting the long-term durability of epoxies are discussed. These factors include the network structure, microvoid characteristics and fabrication stresses, and environmental factors such as service stresses, humidity, temperature, and solar radiation.

Conclusion

TGDDM-DDS epoxies are not highly crosslinked because of steric and diffusional restrictions; they deform and fail predominantly by a crazing process. The durability of TGDDM-DDS epoxies depends on a complex number of interacting phenomena, including sorbed moisture which acts as a plasticizer and a swelling and solvent crazing agent.

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